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(54) Use of beta-cyclodextrin and a method for improving thickeners for aqueous systems.

(57) Methyl-β-cyclodextrin having hydrophobic groups is used for reversibly suppressing the viscosity of an aqueous system containing a hydrophobically-modified thickener.
A method is also provided.

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This invention is concerned with thickeners for aqueous systems and eliminates the need for organic cosolvents. More particularly, the invention relates to use of a β-cyclodextrin to reversibly supress the viscosity of an aqueous system containing a hydrophobically modified thickener. The invention also relates to a method for reversibly suppressing the aqueous system.

Aqueous systems, such as for example coatings containing emulsion polymer binders, typically employ thickeners to obtain the desired degree of viscosity needed for the proper formulation and application of the aqueous system. One general type of thickener used in aqueous systems is referred to in the art by the term "associative." Associative thickeners are so called because the mechanism by which they thicken is believed to involve hydrophobic associations between the hydrophobic moieties on the thickener molecules themselves and/or with other hydrophobic surfaces. A number of different types of associative thickeners are known including, but not limited to hydrophobically-modified polyurethanes, hydrophobically-modified alkali soluble emulsions, hydrophobically-modified hydroxyethyl cellulose or other hydrophobically-modified natural products, and hydrophobically modified polyacrylamides.

Certain of these associative thickeners, such as for example the hydrophobically-modified polyurethane thickeners, are sold as aqueous solutions containing organic cosolvents. The function of the organic cosolvent, such as for example propylene glycol and butyl carbital, is to suppress the viscosity of the aqueous solution containing the associative thickener to allow for ease in its handling before its use as a thickener. While these organic cosolvents perform their intended function, they possess potential environmental, safety and health disadvantages. Viscosity suppression may also be accomplished by the use of surfactants. While this presents no specific health/environmental hazard, it does degrade paint performance.

US-A-5,137,571 discloses a method for reversibly complexing a cyclodextrin compound with the hydrophobic moieties on a hydrophobically modified thickener to suppress the viscosity of the aqueous solution containing the thickener so that such solutions can be easily handled, and then decomplexing the cyclodextrin compound from the thickener to permit the thickener to perform its intended function. The patent discloses that α,β-cyclodextrin, and γ-cyclodextrins can be used effectively to suppress the viscosity of the aqueous solutions of hydrophobically-modified thickeners. They also disclose that hydroxyethyl- and hdroxypropyl-cyclodextrins are preferred to the unmodified versions of cyclodextrin.

The problem with which this invention is concerned is the further improvement of viscosity suppr ssion of an aqueous solution which contains a hydrophobically-modified thickener.

In accordance with the present invention there is provided use of a β-cyclodextrin having hydrophobic groups for reversibly suppressing the viscosity of an aqueous system containing a hydrophobically-modified thickener, characterized in that the β-cyclodextrin is methyl-β-cyclodextrin.

There is also provided a method for reversibly suppressing the viscosity of an aqueous solution containing a hydrophobically-modified thickener, the method comprising the steps of:

i) complexing the hydrophobic moieties on the thickener with a pre-determined amount of a β-cyclodextrin having hydrophobic groups;

ii) adding the complexed thickener and β-cyclodextrin to an aqueous system which is to be thickened; and

iii) decomplexing or desorbing the β-cyclodextrin from the thickener; characterized in that the β-cyclodextrin is methyl-β-cyclodextrin.

The aqueous system is preferably a paint.

The inventors have unexpectedly found the methyl-β-cyclodextrin, a modified version of cyclodextrin, gives superior viscosity suppression as compared to the preferred commercially-available hydroxyethyl cyclodextrin, and even as compared to the most preferred commercially-available hydroxypropyl cyclodextrin.

Cyclodextrin compounds are cyclically-closed oligosaccharides with 6, 7 or 8 α-D-glucoses per macrocycle. The six glucose ring cyclodextrin compound is referred to as an α-cyclodextrin; the 7 glucose ring cyclodextrin compound is referred to as a β-cyclodextrin, and the 8 glucose ring cyclodextrin compound is referred to as a γ-cyclodextrin. Cyclodextrins are produced from starch of any selected plant variety, such as corn, potato and waxy maize. The starch may be modified or unmodified, derived from cereal or tuber origin and the amylose or amylopectin fractions thereof. The selected starch in the form of an aqueous slurry, at concentrations up to about 35% by weight solids, is usually liquefied, by gelatination or by treatment with a liquefying enzyme such as bacterial α-amylase enzyme, and then subjected to treatment with a transglycosylate enzyme to form the cyclodextrins. The amount of individual α,β and γ cyclodextrins will vary depending on the selected starch, selected transglycolase enzyme and processing conditions. Precipitation and separation of the individual cyclodextrins is described in the literature using solvent systems, inclusion compounds such as trichloroethylene and non-solvent systems utilizing selected ion exchange resins. β-cyclodextrin is the most widely used form and is known for use in the production of pharamaceuticals and foods.

The ability of cyclodextrins to form inclusion complexes with organic compounds and thereby increase the water solubility of the organic compound is known. In "Cyclodextrins Increase Surface Tension and Critical

Micelle Concentrations of Detergent Solutions" by W. Saenger and A. Muller-Fahrnow, *Agnew. Chem. Int. Ed. Egl* 27 (1988) No. 3 at pages 393-394, the authors discuss the ability of the central hydrophobic cavity of the cyclodextrin compounds to accommodate the hydrophobic, aliphatic part of a detergent molecule having a diameter of about 5 Angstroms. Studies with such detergents showed that the cyclodextrins were capable of increasing the surface tension of the detergent molecule and shifting the critical micelle concentration of the detergent to a example to avoid foaming.

U.K. Patent Application 2,189,245A discloses a method for increasing the water solubility of cyclodextrins. This method involves modification with alkylene carbonates and preferably ethylene carbonate to form hydroxyethyl ethers on the ring structure.

Because cyclodextrin compounds absorb on to or form complexes with hydrophobic species, they can be absorbed on to the hydrophobic moieties of associative thickeners. The absorption of cyclodextrin compounds on to the hydrophobic moieties of associative thickeners causes a suppression of the viscosity of an aqueous solution containing the associative thickener. Cyclodextrin compounds can be readily desorbed or decomplexed from the associative thickener by the addition of another material which has an affinity for the cyclodextrin.

The water solubility limit of methyl-β-cyclodextrin is about 80 grams per 100 grams of water. This limits the concentration of methyl-β-cyclodextrin which can be employed to suppress the viscosity of an aqueous solution containing an associative thickener. Since the viscosity of an aqueous solution containing an associative thickener increases with the concentration of the associative thickener solids, the solubility limit of the methyl-β-cyclodextrin determines the maximum amount which can be added to the solution without resulting in the formation of undesirable solids. If the maximum concentration of the methyl-β-cyclodextrin needed to reduce the viscosity of an aqueous solution containing an associative thickener to a handleable viscosity, such as for example a viscosity of about 2,000 centipoises, exceeds the solubility limit of the methyl-β-cyclodextrin in water, then the methyl-β-cyclodextrin is not effective as a viscosity suppressant additive. In other words, the effectiveness of the methyl-β-cyclodextrin as a viscosity suppressing additive is a function of the solubility limit of the methyl-β-cyclodextrin and the solids content of the associative thickener in the aqueous solution. The higher the solids content of the associative thickener the higher the viscosity of the aqueous solution containing it will be, and likewise the higher the concentration of the cyclodextrin which will be needed to be added to suppress the viscosity down to a level where it easily flows.

The inventors have found that the use of methyl-β-cyclodextrin is useful in latex paint formulation for achieving a variety of effects, such as for example:

- to permit the preparation and supply of a low viscosity, high solids solution of the thickener without the use of viscosity suppressing solvent;
- to ease incorporating hydrophobically modified, associative thickeners, having marginal solubility in water, into aqueous systems;
- to reduce the viscosity drop of associative thickener containing formulations upon the addition of colorants or surfactants to the formulation;
- to improve the efficiency of the associative thickener itself, thus reducing the thickener required to reach a given paint viscosity;
- to reduce foaming in a paint, with or without an associative thickener, which is especially desirable when the paint is to be applied by a roller; and
- to reduce the color development problems caused by surfactants in some formulations.

The ability to decomplex the methyl-β-cyclodextrin from the hydrophobic associative thickener is just as important as the ability of the methyl-β-cyclodextrin to absorb or complex with the associative thickener in the first instance. It is critical for the thickener to perform its intended viscosity increasing function in the aqueous system to which the associative thickener solution is added that the cyclodextrin becomes decomplexed or desorbed from the hydrophobic moieties on the associative thickener molecule. We have found that methyl-β-cyclodextrin is readily desorbed or decomplexed from hydrophobic associative thickeners simply by the addition of a material which has an affinity for the cyclodextrin. In this regard, we have found that conventional surface active agents commonly present in aqueous coating systems including, anionic surfactants such as sodium lauryl sulfate, nonionic surfactants such as IGEPAL® CO-660 (a 10 mole ethoxylate of nonyl phenol), and cationic surfactants, may be used to decomplex or desorb the cyclodextrin. Other water soluble organic solvents such as for example ethanol and TEXANOLO® solvent may also be employed for this purpose but are not preferred. The inventors have found that it is preferred to utilize about one mole of the decomplexing agent p r mole of the methyl-β-cyclodextrin added to the associative thickener solution to achieve complete d sorption or decomplexation.

Both the compl xation and decomplexation mechanisms are easily achieved by the addition of the reactants with mixing. No special purification or separation steps are required at room temperature. It is not nec-

essary to add additional surfactant to cause this decomplexation process to occur: for example, the formulation surfactants already present in paint have been found to be sufficient.

The surfactant complexing effect of the cyclodextrins are also of benefit to the formulator for properties other than rheological modification. Typically when formulating tinted paints, the composition of the formulation, specifically the surfactants, must be modified to maintain the stability of the colorant dispersion while not adversely affecting the dispersion of the other components. In some formulations, the paint components, such as the latex vehicle, bring an incompatible surfactant into the formulation. To correct this, additional surfactants are added to the formulation to compatibilize the system. While effective in compatibilizing the system, these surfactants can contribute adverse water sensitivity and foaming characteristics to the formulation. Methyl-β-cyclodextrin is useful in improving the compatibility of a colorant without adding additional surfactants.

The invention will now be described by way of example:

EXAMPLE 1. THICKENERS IN WATER

The methyl-β-cyclodextrin was tested to demonstrate that it suppressed the viscosity of an hydrophobically-modified thickener in water better than preferred commericially-available hydroxyethyl cyclodextrin and most preferred commericially-available hydroxypropyl cyclodextrin.

4.9 grams of each cyclodextrin material were mixed with 77.6 grams of water and then 17.5 grams of ACRYSOL® RM-8 solid grade hydrophobically modified polyurethane thickener was added and mixed. The low shear viscosity of the resultant mixture was measured using an Brookfield viscometer. The results are reported in Table 1.1 in centipoises.

Table 1.1

	Viscosity (centipoises)
Methyl-β-cyclodextrin (Wacker)	802
Comparatives	
Hydroxypropyl-α-cyclodextrin HP 0.6 (Wacker)	19,200
Hydroxypropyl-β-cyclodextrin HP 0.9 (Wacker)	5,240
Hydroxypropyl-β-cyclodextrin (American Maize)	2,820
Hydroxypropyl-γ-cyclodextrin HP 0.6 (Wacker)	>100,000

EXAMPLE 2. THICKENERS IN PAINT FORMULATIONS

Paints with hydrophobically modified thickener complexed with cyclodextrin materials were formulated to demonstrate that the methyl-β-cyclodextrin does not adversely affect the other properties of the paint formulation as compared to the other cyclodextrin materials.

The ingredients in Table 2.1 (in grams) were used to formulate the paints. In a container, the grind ingredients were first mixed together at high speed with Cowles dissolver and then the letdown ingredients were added and mixed at a low speed. In a separate container, the cyclodextrin material and appropriate water portion were mixed together and then the thickener was added and mixed until homogeneous. The complexed thickener mixture was then added to the grind and letdown mixture.

The anionic surfactant present in the paint formulations was sufficient to decomplex the cyclodextrin materials from the thickener. Therefore, no additional surfactant needed to be added to the formulations.

Table 2.1

Ingredient	Paint 1	Paint 2*	Paint 3*	Paint 4*	Paint 5*	Paint 6¥
Grind						
Water	45.00	45.00	45.00	45.00	45.00	45.00
Coalescent (propylene glycol)	70.00	70.00	70.00	70.00	70.00	70.00
Dispersant (Tamol® SG-1) (35%)	12.35	12.35	12.35	12.35	12.35	12.35
Antifoaming agent (Foamaster VL)	1.00	1.00	1.00	1.00	1.00	1.00
Titanium dioxide (Ti-Pure® R-900)	209.99	209.99	209.99	209.99	209.99	209.99
Extender (ASP-170)	88.02	88.02	88.02	88.02	88.02	88.02
Letdown						
Water	116.70	116.70	116.70	116.70	116.70	116.70
Acrylic latex emulsion (Rhoplex® AC-264) (60.5% solids)	378.00	378.00	378.00	378.00	378.00	378.00
Coalescent (Texanol®) (2,2,4-trimethyl-3-hydroxypentyl acetate)	11.43	11.43	11.43	11.43	11.43	11.43
Antifoaming agent (Foamaster VL)	3.00	3.00	3.00	3.00	3.00	3.00
Thickener/Cyclodextrin						
Hydrophobically-modified Polyurethane Thickener (100% solids)	1.67	1.71	1.66	1.38	1.33	1.68
Water	132.58	132.27	132.33	132.69	132.76	131.52
Cyclodextrin (solid grade)						
Methyl-β-cyclodextrin (Wacker)	0.41	-	-	-	-	-
Hydroxypropyl-α-cyclodextrin (Wacker)	-	0.48	-	-	-	-
Hydroxypropyl-β-cyclodextrin (Wacker)	-	-	0.47	-	-	-
Hydroxypropyl-β-cyclodextrin (American Maize	-	-	-	0.39	-	-
Hydroxypropyl-γ-cyclodextrin (Wacker)	-	-	-	-	0.37	-
Butyl carbitol	-	-	-	-	-	1.26

*Comparatives
¥Control (no cyclodextrin premixed with thickener)

EXAMPLE 3. TESTING OF THICKENERS IN PAINT FORMULATIONS

Several tests were performed to demonstrate that while the method of the present invention gives superior viscosity suppression as compared to other cyclodextrin materials, the method of the present invention does not detrimentally affect other properties of the paint formulation.

EFFICIENCY

The efficiency of the thickener which had been complexed with a cyclodextrin material was measured by determining the amount of dry pounds of thickener that was required to thicken 100 gallons of the paint formulation to about a targeted 95 Krebs Units stormer viscosity. The efficiency data are reported in Table 3.1 in dry pounds.

ICI VISCOSITY

The high shear viscosity of the paints were measured using an ICI Viscometer. The viscosity measurements are reported in Table 3.1 in poise.

LENETA FLOW

The flow and leveling of each paint were determined. Each paint was applied to a separate Leneta sealed 12H chart at 25°C and positioned horizontally to dry overnight. The dried charts were compared to reference standards in a Leneta Level-Luminator. The flow and leveling results are reported in Table 3.1 as the number of the reference standard which most nearly matched the appearance of each paint.

LENETA SAG

The sag of each paint was determined. Each paint was applied with a drawdown bar to a separate Leneta sealed 12H chart having a water-soluble ink line (drawn perpendicular to the length of the chart) at 25°C and hung vertically to dry overnight. The dried charts were rated by the highest thickeness (measured in mils) at which the paint sagged beyond the water-soluble ink line by less than 0.5 centimeter. The sag results are reported in Table 3.1.

GLOSS (60° and 85°)

The gloss of each paint was measured. Each paint was drawndown on a Leneta 5C chart with a 3 mil Bird film applicator and dried at constant temperature and humidity for 7 days. The gloss of each paint was measured on a Hunter Glossmeter at 60° and 85°, according to ASTM D-523-89 Test Method. The gloss results are reported in Table 3.1.

COLORANT STABILITY

The stability of each paint was measured before and after the addition of 2 ounces/gallon of Lamp Black colorant with a Krebs-stormer viscometer. The viscosity results and the delta values are reported in Table 3.1.

HEAT AGE STABILITY

The stability of each paint was measured before and after heat aging at 140°F for 10 days with a Krebs-stormer viscometer. The viscosity results and the delta values are reported in Table 3.1.

Table 3.1

	Paint 1	Paint 2*	Paint 3*	Paint 4*	Paint 5*	Paint 6¥
Effieciency (dry pounds/100 gallons paint)	1.38	1.71	1.66	1.33	1.47	1.68
Sormer Viscosity (KU)	93	96	96	96	96	96
ICI Viscosity (poise)	0.6	0.6	0.7	0.6	0.6	0.6
Leneta Flow	9	9	9	9	9	9
Leneta Sag		8	8	8	8	88
Gloss						
60°	40	39	40	40	39	39
85°	88	86	88	87	86	88
Color Stability						
Initial Stormer Viscosity (KU)	101	106	106	106	106	106
Final Stormer Viscosity (KU)	80	83	83	83	83	83
Delta (KU)	-21	-23	-23	-23	-23	-23
Heat Age Stability						
Initial Stormer Viscosity (KU)	101	106	106	106	106	106
Final Stormer Viscosity (KU)	109	110	109	110	114	118
Delta (KU)	+8	+4	+3	+4	+8	+12

*Comparatives
¥Control (no cyclodextrin premixed with thickenr)

Claims

1. Use of methyl-β-cyclodextrin as a β-cyclodextrin having hydrophobic groups for reversibly suppressing the viscosity of an aqueous system containing a hydrophobically-modified thickener.

2. Use as claimed in claim 1, wherein the aqueous system is a paint.

3. A method for reversibly suppressing the viscosity of an aqueous solution containing a hydrophobically-modified thickener, the method comprising the steps of:
   i) complexing the hydrophobic moieties on the thickener with a pre-determined amount of a β-cyclodextrin having hydrophobic groups;
   ii) adding the complexed thickener and β-cyclodextrin to an aqueous system which is to be thickened; and
   iii) decomplexing or desorbing the β-cyclodextrin from the thickener; characterized in that the β-cyclodextrin is methyl-β-cyclodextrin.

4. The method of claim 3, wher in the hydrophobic thick ner is s lected from the group consisting of hydrophobically modifi d poly thoxylat d urethanes, hydrophobically modifi d alkali solubl mulsions, hydrophobically modified hydroxy thyl cellulose and hydrophobically modifi d polyacrylamides.

5. The method of claims 3 or 4, wherein the methyl-β-cyclodextrin is decomplexed or desorbed from the

thickener by addition of a pre-determined amount of an anionic, nonionic or cationic surfactant.

6. The method of claim 5, wherein the surfactant is added to the aqueous system at a concentration of one mole per mole of methyl-β-cyclodextrin.

7. The method as claimed in claims 3, 4, 5 or 6, wherein the aqueous system is a paint.

8. A paint or other thickened aqueous system comprising hydrophobically-modified thickener and methyl-β-cyclodextrin having hydrophobic groups as a β-cyclodextrin viscosity suppressant.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 1448

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
A,D	EP-A-0 460 896 (ROHM AND HAAS) * claims 1-15 * -----	1-8	C09D7/00 C09D105/16
			TECHNICAL FIELDS SEARCHED (Int.Cl.5)
			C09D C08L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 June 1994	Beyss, E

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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